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IONIC LIQUIDS IN THE SOLVENT EXTRACTION OF PLATINUM-GROUP METALS – HOW FAR CAN THEY GO?

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ABSTRACT
Ionic liquids (ILs) are molten salts that are liquid at room temperature. Although their existence has been known from the beginning of the 20th century, only at the end of the 80's – beginning of 90's their characteristic properties and potential advantages began to be widely explored. Nowadays there is no doubt that ILs have become a major subject of research for modern chemistry, and the industry progressively starts to include ILs in chemical processes. This communication presents and discusses some relevant results found in literature concerning the application of ILs to recover platinum-group metals (PGMs) from complex leaching solutions by solvent extraction (SX). Based on the available data, an evaluation about the forthcoming of ILs to recover PGMs from real leaching solutions of spent catalysts will be assessed.

Keywords: Ionic liquids; solvent extraction; platinum-group metals; chloride leaching solutions

INTRODUCTION
An ionic liquid (IL) is a salt with a melting temperature below the boiling point of water, or more typically, it is in the liquid phase at room temperature. Most ILs contain a larger organic cation and a comparatively smaller inorganic anion, and this particular feature promotes unique solvent properties for these materials, providing them with an unusual range of temperatures between the freezing and boiling points. This attribute puts ILs in the path of the best non-volatile organic solvents known to date, therefore, ILs are aligned with the "green chemistry" principles as being the required solvents for a sustainable future [1]. Furthermore ILs have low vapor pressure, are non-flammable, and display excellent chemical/electrochemical/thermal stabilities, favorable characteristics to long-term operation processes [2].
The miscibility of ILs with water or organic solvents depends on the size of the substituents of the cation and on the choice of anion. Moreover, ILs often show favourable solvating properties for a range of polar and non-polar compounds [1]. Accordingly, the necessary hydrophobic features an IL should exhibit to be immiscible with aqueous phases, and consequently be used in hydrometallurgical solvent extraction (SX), can be conveniently designed and adjusted as required.
The hydrometallurgical recycling of platinum-group metals (PGMs) from leaches of secondary resources often include SX as the most adequate separation technique [3]. Traditional SX consists of two stages, extraction and stripping. Successful SX processes effectively separate the metal of interest from impurities, left in the aqueous raffinate, and also make feasible the reutilization of the solvent. A final recovery stage is required to achieve the metal itself or an appropriate metal salt.
As ILs are increasingly investigated to replace the conventional organic solvents in several applications, it is not strange that their suitability to work in the SX of PGMs as unique solvents or only as extractants (requiring the addition of a proper diluent) may be progressively arising in literature [2]. This latter option obviously compromises the "greenness" of the SX process while surpassing the usual drawbacks of the relatively high viscosity of the ILs and high associated costs.

PGMs continue to be considered as critical raw materials by the European Union in the last report available [4]; hence, the development of PGMs recycling practices from end-of-life materials should be a commitment felt by all the intervenient parts [3]. Therefore, this communication aims to point out some of the most relevant collected issues focusing on the use of ILs to recover PGMs from chloride leaching solutions of spent catalysts, particularly platinum, palladium and rhodium.

IONIC LIQUIDS IN THE SOLVENT EXTRACTION OF PGMs

The structures of the main cations and anions included in commercial ILs that have been investigated for the SX of Pt, Pd and Rh are depicted in Fig. 1. The usual tradenames or abbreviations used for the ILs or for the constituent ions are also indicated.

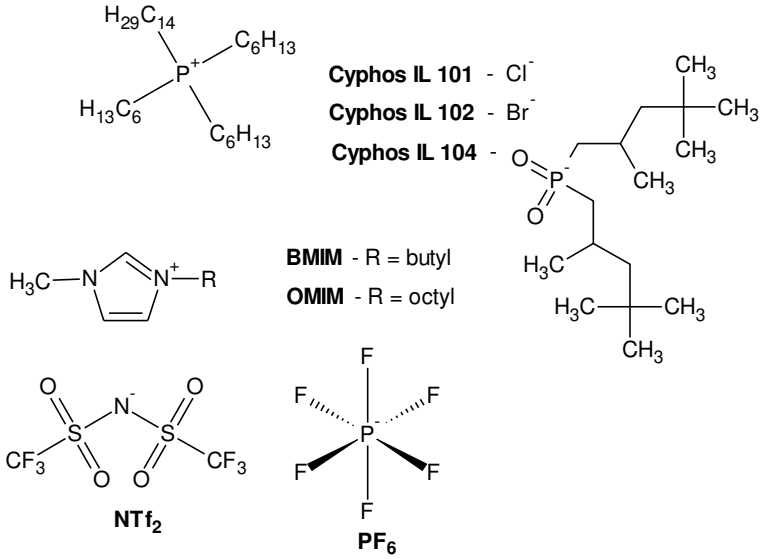

Figure 1 – Structures of the main cations and anions in ILs, investigated for the SX of PGMs.

All Cyphos ILs are composed by the phosphonium cation displayed in Fig. 1, their diverse designations being related with the different anions. Other ILs have the 3-methylimidazolium cation with a butyl (BMIM) or octyl group (OMIM) in position 1, associated with either the bis (trifluoromethylsulfonyl) imide (NTf_2) or hexafluorophosphate anions (PF_6).
Some of the main collected data reported so far is summarized in sequence.

ILs in a diluent

When dissolved in toluene, *e.g.* [5], or in xylene [6], Cyphos 101 is able to efficiently co-extract Pd(II) and Pt(IV) from 0.1M HCl, with a good selectivity over Ni(II), Cu(II), Pb(II), Fe(III), Rh(III) and Ru(III) [5]. These figures generally become worse for higher HCl concentrations. Aqueous ammonia to strip Pd(II) [5] or a selective Pt(IV) stripping by NaSCN followed by thiourea in HCl to recover Pd(II) from the organic phase [6] proved to be efficient. The extractive performance shown by Cyphos 104 is relatively similar to that verified for Cyphos 101 [5, 7]. Furthermore, the kinetics of extraction and stripping are favorable (less than 10 min).
Cyphos 102 in toluene is even more efficient to extract Pd(II) and Pt(IV) than the previous ones, e.g. [8, 9], maintaining its performance even for 5M HCl as feed phase. Rh(III) is extracted at 40-50% under the same conditions.

ILs as solvents

Undiluted Cyphos 101 and 102 extract 89.7 to 99.9% Pd(II) until 8M HCl. Both ILs are also able to extract Rh(III) satisfactorily until 4M HCl, particularly Cyphos 102. Hence, Pd(II) can be effectively separated from Rh(III) from aqueous solutions containing at least 6M HCl [10]. Contact times of 24h were considered and stripping was not evaluated, since authors intend to explore the possibility of carrying out the electrodeposition of the metals directly from the loaded organic phases.

The IL [OMIM] [NTf_2] [11, 12] extracts > 85% Pt(IV) from 1M HCl, being able to effectively separate Pt(IV) from Pd(II) from 2M HCl, as Pd(II) is traceably extracted at the latter HCl concentration. The mixture [OMIM] [NTf_2] and Cyphos 101 increases Pt(IV) extraction significantly, from 1M HCl and for a 3h contact, Pt(IV) stripping being effectively accomplished by 2M HNO_3. Good recyclability profiles for Pt(IV) in five successive extraction-stripping stages are also described [13].

The general efficiency and selectivity data found in literature are promising, but the SX of PGMs by ILs is still in its infancy. The potential is enormous, novel approaches will surely have to be considered and developed, probably also extended to new types of chemical reactors [14]. To the best of our knowledge, ILs have not been tested with real leaching solutions of spent catalysts to date.

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